201-16326

Petroleum HPV

August 14, 2006

The Honorable Stephen L. Johnson
U. S. Environmental Protection Agency
P. O. Box 1473
Merrifield, VA 22116

Attention: Chemical Right-to-Know Program

HPV Challenge Program, AR-201
HPV Consortium

Re: Response to Comments on Petroleum HPV Testing Group's Asphalt Category Test Plan

Dear Administrator:

The Petroleum HPV Testing group is a consortium representing 92 percent of the nation's refining capacity. The Group is made up of 60 member companies of the American Petroleum Institute (API), the National Petrochemical and Refiners Association (NPRA), the Gas Producers Association (GPA) and/or the Asphalt Institute. The Testing Group appreciated the comments received on its Test Plan for the Asphalt Category that was submitted on December 15, 2003 and posted on the Agency's ChemRTK website on January 20, 2004. The Environmental Protection Agency (EPA), the Environmental Defense (ED) and the Physicians Committee for Responsible Medicine (PCRM) submitted comments on this Test Plan. In the interest of communicating our intent with all interested stakeholders, the Testing Group is providing a revised test plan and robust summaries for posting on the ChemRTK website. In addition, the two sets of documents will be posted on our website, www.petroleumhpv.org. Below is a summary of the comments received and our response.

Category Justification

EPA commented that available data on physicochemical properties, environmental fate and toxicity support the grouping of these substances into a single category. However, ED stated that there was not sufficient information on the composition of the category members to justify a single category and wanted to know if the variability of composition influenced the pattern of toxic response for each of the proposed members.

> The Testing Group believes that a single HPV category for these six asphalt manufacturing process streams is justified. Appendix 2 of the test plan provides an overview of the manufacturing steps from Crude Oil to blended asphalt products. Asphalt products that leave the refinery meet specifications that ensure common physicochemical properties and use patterns. The variability of metals (vanadium, nickel) or sulfur content in the whole asphalt is primarily a reflection of the crude oil source but they are not present in significant concentration in the fume condensate. Therefore their influence on mammalian toxicity is expected to be negligible. The additional data in the revised test plan reinforces our conclusion that those components also do not contribute to ecotoxicity (Kriech, et al, 2005).

The Agency did not think the Testing Group had addressed/considered the potential toxicity of metals for all category members.

> Low levels of various metals would be expected to be present in all category members. The concentrations found in commercial asphalt products are dependant upon the source of crude oil (Magaw, et al, 2000; SHRP, 1993; Kriech et al, 2005). In a recent study, principal trace-level elements detected in 10 commercial paving and roofing asphalts showed average concentrations of 270 ppm vanadium, 72 ppm nickel, 31 ppm iron, 25 ppm sodium, 3.7 ppm zinc 1.9 ppm molybdenum and 1.9 ppm titanium. Other elements were detected at levels <1 ppm (Kriech et al, 2005). Except for one heavy crude oil source (Boscan), the concentrations of the two most predominate metal species, vanadium and nickel, rarely exceeded 300 and 150 ppm, respectively. This new analytical information on metals has been incorporated into Table 2 of the revised Test Plan. Further, metals are not easily extracted from asphalt as evidenced by several leachability studies. These studies have shown that metals in asphalt leachate water are either below detection limit values or in the low part-per-billion range (Kriech 1990; Kriech 1992; Kriech, et al, 2005).

Physicochemical Properties

Vapor Pressure EPA does not recommend further testing, but suggests that the submitter provide in the robust summary a range of vapor pressures for potentially volatile components.

> The robust summary for vapor pressure was revised to include estimates for representative paraffinic, naphthenic, and aromatic constituents covering C-range of 25 to 50. Estimates also were given for specific PAH components. The vapor pressure section in the Test Plan has been revised accordingly.

Water Solubility EPA does not recommend further testing, but suggests that the submitter provide in the robust summary the water solubility of PACs detected in leachate samples or a range of water solubility for each of the PACs classes identified.

> An additional comment section (Section 2.14) was added to the robust summaries that provided water solubility values for the PACs screened in the Brandt and DeGroot (2001) leachate study. A new Kriech et al. (2005) study was added to the Robust Summary. The water solubility section in the Test Plan has been revised accordingly to add the new Kriech et al. (2005) data.

Environmental Fate

Photodegradation EPA agrees that the majority of components will not partition to air. However, asphalts are heated during their application and EPA suggested that the submitter provide a range of photodegradation half-lives for PAHs found in asphalt fume condensate.

> A range of estimate half-lives for representative compounds and PACs have been put in the robust summary. The photodegradation section of the Test Plan has been revised accordingly.

Health Effects

General
ED asked that the Testing Group provide information regarding the concentration of hydrogen sulfide (H_2S) that may be present in the proposed test material and whether that level will be representative of all category members.

> H_2S generation is primarily a function of heated storage conditions (time and temperature) and is not related to the asphalt type being stored. H2S is not found in any appreciable quantity in freshly generated asphalt fume (Gamble et al., 1999).

ED wanted to know the temperature used to produce asphalt at the asphalt plant and the temperature at which the asphalt is applied to roads or roofs.

> Basic information concerning the temperatures used in the manufacture and commercial application of the various asphalt products is provided in Appendix 2 & 3 of the test plan. Simply stated, paving asphalt is applied at a temperature not to exceed 325 F. The temperature at the point of application of roofing asphalt is approximately 330-445 F (Asphalt Institute, 1990).

ED also noted that asphalt is prepared by different methods: batch and drum. ED wanted to know whether the temperatures used were the same or different and are there different amounts of pollutants emitted from batch and drum plants.

> Paving asphalt is made by mixing mineral aggregate and asphalt (20:1) at hot mix asphalt (HMA) plants by either the batch or drum method at typical temperature ranges of 250 to 325 F (not to exceed 350 F). The volatiles released at HMAs are captured by an emission control system (called the baghouse) and are limited by applicable air pollution permits. Asphalt fume emissions from HMA plants are significantly lower than industrial hygiene monitoring measurements taken on workers during end use paving and roofing applications (Gamble et al, 1999).

Acute Toxicity
EPA stated that the submitter needs to indicate whether the administered concentration, (100 mg/m3) in the Fraunhofer, (2000) study, is close to the maximum achievable concentration.

> The Fraunhofer study did not determine the maximum achievable concentration. In the study report (Fraunhofer, 2000), the researchers stated that the high-dose target concentration of 100 mg/m3 (Total Hydrocarbon Concentration) was 5 times the current German occupational exposure limit (20 mg/m3) for indoor working with hot bitumen. The actual high-dose concentration in the study as measured by IR according to BIA [Germany] guideline #6305 and corrected for aromatic content was 149.17 mg/m^3 total hydrocarbon of bitumen fumes (Ekström et al., 2001).

Repeated-Dose Toxicity
ED stated that the OECD 413 rat inhalation repeat dose toxicity study with bitumen paving fume appears to be well-conducted, but the composition of the test substance, other than PAHs, was not provided in the robust summary.

No additional information on the sample composition is available. Information on the Total Hydrocarbon Concentration (THC) including vapor/aerosol ratios has been added to the robust summary.

EPA recommended changing the reliability rating from A1 – reliable without restriction to A2-Reliable with restrictions, for the rabbit dermal repeat dose toxicity study with vacuum residue. The EPA felt this change was needed to reflect the fact that the rabbits in the study were exposed for only 3 days per week, a No-Observed-Adverse-Effect-Level (NOAEL) was not achieved, and an encephalitozoon infection may have confounded the test results.

In light of EPA's comments, the Test Group has changed the reliability rating of these studies from A1 to A2.

EPA also noted the highest dose listed in the table of the total weight gain results (rabbit dermal study - page 18/45) should be 2000 mg/kg/day instead of 200 mg/kg/day.

The dose in the total weight gain table was corrected to be 2000 mg/kg/day.

Genetic Toxicity
EPA requested the Test Group provide full robust summaries for one or more of the in vitro and in vivo studies on asphalt fume condensates, to satisfy the chromosomal aberration endpoint. Alternatively, the agency asked the Test Group to provide a robust summary for the micronucleus evaluation testing being conducted by Fraunhofer ITA (2002) as part of a 2-year inhalation bioassay in rats on bitumen paving fumes (page 15, test plan).

A robust summary of an *in vivo* micronucleus assay has been provided in the revised test plan (Ma, et al., 2002). The Testing Group will submit a robust summary of the micronucleus assay when the Fraunhofer 2-year study of bitumen paving fume has been completed.

EPA observed that in the robust summaries for two bone marrow cytogenetic assays in rats with vacuum residue (Ref. 7), the units for the doses listed in the tables should be g/kg/day instead of mg/kg/day.

The dose levels in the robust summaries have been corrected to g/kg/day.

Reproductive/Developmental Toxicity
PCRM did not agree with the Testing Group's proposal to conduct a reproductive-developmental toxicity study. They felt that the weight of evidence indicates that asphalt fume would have minimal potential for reproductive/developmental toxicity.

No developmental or reproductive toxicity studies on asphalts or asphalt fumes are available. Existing subchronic studies with asphalt fume condensate have been done with material generated at temperatures used in paving operations (<325°F). No studies with asphalt fume condensate collected to simulate typical end-use temperatures (<445°F) used in roofing operations have been done. Therefore the Testing Group has reevaluated the recommendations made in the original test plan submission and proposes to conduct an OECD 422 and OECD 474 to evaluate subchronic, reproductive/developmental, and in vivo

> cytogenetic effects. A roofing asphalt fume condensate will be used because it is generated at a significantly higher temperature and is appropriate to "bound" the fume composition from all members of the asphalt category. The Testing Group believes it is acting responsibly to address this issue by selecting a single test sample to represent the six materials in the test plan and by conducting an OECD 422 and OECD 474 in the same animals to cover mammalian HPV endpoints with the fewest number of animals.

EPA and ED agreed with the submitter's proposal to conduct a combined reproductive - developmental toxicity screening test on asphalt fume condensate. EPA recommended using fumes generated under conditions that maximize the level of PACs to represent a worst-case scenario.

> Because asphalt roofing operations use the highest recommended end-use temperature, roofing asphalt will be the source for the fume condensate sample that is tested. The Testing Group will use a fume condensate sample that has been determined to be compositionally similar to fume present at current US roofing operations (McCarthy et al., 1999; Fraunhofer, 2003; 2004; Kriech et al., 2002; Kriech, 2006ab)

ED asked how the test material in the proposed reproductive developmental toxicity would be selected. Which of the six proposed category members will be selected? If only one sample is selected, what will be the criteria for sample selection?

> The category contains three CAS numbers for end-use products and three for intermediate process streams. Two CAS numbers, i.e., asphalt and oxidized asphalt, represent >99% of the end-use materials (paving asphalt (84%) and roofing asphalt (15%) (AI, 1990). The Testing Group collected fumes from the predominant grade of paving asphalt and the predominant grade of roofing asphalt in the US and compared their physical properties and compositional differences (Kriech 2006ab). The Testing Group proposes to test the roofing asphalt fume condensate because it is generated at a significantly higher temperature and is therefore appropriate to "bound" the fume composition from all members of the asphalt category.

Ecological Effects

EPA agrees with the use of analog data to satisfy the ecological effects endpoints for the asphalt category. The analog data provided are considered worst-case scenario, in that asphalt category members are more water-insoluble than the analogs. Therefore, asphalt category members are not likely to show adverse acute or chronic ecological effects in aquatic species. One limitation of the analog data, however, is that all aquatic tests referenced were performed using water-accommodated fractions (WAF) rather than measured data using HPLC analytical or equivalent techniques.

> It is the Test Group's opinion that the use of water-accommodated fractions is adequate and widely accepted for the assessment of the aquatic hazards of petroleum hydrocarbon mixtures. For the assessment of the ecotoxicity of poorly water soluble mixtures of hydrocarbons as found in petroleum products, the generally accepted procedure is to report results expressed in terms of the "loading rate" (OECD 2000). The loading rate is defined as the amount of the product that is equilibrated with the aqueous test medium. The

aqueous phase at equilibrium is termed the water accommodated fraction (WAF) for the specific loading rate. Toxicological endpoints such as the LL50 or EL50 are determined to express the loading rate of the test material that is lethal to or produces a specific effect in 50% of the test organisms. Given the extremely low water solubility of constituent hydrocarbons in asphalt materials, it is unlikely that standard analytical techniques would be sufficiently sensitive when applied to aquatic dose-response studies using a maximum loading rate of 1000 mg/l. The referenced leachability studies confirmed at much higher asphalt /water loading rates that very little of the constituents in asphalt partition to the water phase.

ED took exception to the argument for no aquatic toxicity testing, and stated the following:

"The sponsor claims that no ecotoxicity tests are needed because asphalt is not expected to be toxic to fish, aquatic invertebrates and algae. The basis for this claim is that asphalt linings have been applied to aquaculture ponds without adverse effects on fish, and that lubricating base oils are nontoxic. However, the chemical compositions of the asphalt used in the linings and the lubricating oil surrogate are not provided. Unless the sponsor can present a more compelling case that existing data are relevant to predicting the ecotoxicity of all six members of the proposed category, ecotoxicity studies need to be conducted at least on the most toxic of the category members (and its selection needs to be justified)."

The Test Group continues to believe and EPA has concurred that the analog data and technical rationale presented in the Test Plan supports the conclusion that substances in the asphalt category present a low ecotoxicity potential. These data include ecotoxicity endpoints covering fish, aquatic invertebrates and algae for the Petroleum HPV categories of lubricating oil basestocks and aromatic extracts. These were chosen as analog data for the asphalt category because:

- Substances in the lube oil and aromatic extract categories are comprised of similar alkyl and aryl hydrocarbon classes that exist in members of the asphalt category,
- The range of carbon numbers making up the constituent hydrocarbon molecules in the lubricating oil basestocks and aromatic extracts (i.e., C15-C50 and C15-C54, respectively) include those that exist in asphalt (i.e., C25-C50) as well as lower molecular weight constituents believed to be even more water soluble, and
- The substantial database of ecotoxicity endpoint values offered in the lubricating oil basestocks and aromatic extracts categories has shown the low ecotoxicity potential of petroleum hydrocarbons in both acute and chronic exposure studies.

The analog data presented in the test plan in conjunction with analytical characterizations of asphalt leachate warrant a conclusion that substances in the asphalt category pose a low potential for adverse effects to aquatic organisms.

New References Cited In This Letter And Added To The Revised Test Plan

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Closing Remarks

The Test Group appreciates EPA's, ED's and PCRM's comments and interest in the Asphalt testing program. It believes that the revised test plan, being submitted via this letter, is both scientifically sound and meets the spirit of the EPA's guidance on animal welfare. The revised test plan makes every effort to minimize the number of animals used in toxicity testing, while at the same time allowing the sponsors to fulfill their product stewardship responsibilities.

The revised Asphalt Category Test Plan and Robust Summaries have been submitted to the EPA ChemRTK electronic mailbox.

If you have any questions or require further information regarding this submission please contact me.

Sincerely,

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Attachments: Revised Asphalt Category Test Plan, 14 August 2006
Revised Asphalt Category Robust Summaries, 2 February 2006